Pauli-Limited Superconductivity in Small Grains

M. C. Bønsager and A.H. MacDonald
Department of Physics, Indiana University, Bloomington, Indiana 47405
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We report on an exploration of the mean-field phase diagram for Pauli-limited superconductivity in small metallic grains. Emphasis is placed on the crossover from the ultra-small grain limit where superconductivity disappears to the bulk thin-film limit as the single-particle level spacing in the grain decreases. We find that the maximum Zeeman coupling strength compatible with superconductivity increases with decreasing grain size, in spite of a monotonically decreasing condensation energy per unit volume.

I. INTRODUCTION

Mesoscopic physics may be broadly defined as the study of phenomena which depend fundamentally on the finite-size of a system, even when that size substantially exceeds characteristic length scales associated with microscopic degrees of freedom. By this definition, recent experiments[1–3] in which strong parity effects are seen in superconducting islands containing $\sim 10^9$ electrons highlight the robustness of superconductor mesoscopics; pairing physics[4,5] causes observable differences between metallic grains with 10^9 electrons and grains with 10^9+1 electrons. Recent progress has enabled studies of much smaller systems. Ralph, Black, and Tinkham[6–8] have demonstrated that it is possible to make single-electron transistors with superconducting islands that are only a few nanometers in radius. These systems contain only $\sim 10^4$ to 10^5 electrons and have a mean energy level spacing δ which can be larger than or comparable to Δ_0, the zero-temperature superconducting gap in bulk samples. As early as in 1959 Anderson observed[9] that superconductivity cannot occur in small grains when the limit $\delta \sim \Delta_0$ is reached. Experimental realization of such ultra-small systems has opened the physics of superconductivity in this regime to experimental study and inspired substantial theoretical interest.[10–15] Many aspects of the experiments can be qualitatively understood using the simplest possible BCS model of an ultra-small grain in which the levels are assumed to be equally spaced and pairing is assumed to occur only between identical orbitals.[16] In this paper we address the influence of Zeeman coupling on superconductivity in such a model, emphasizing the crossover between the ultra-small grain regime and the bulk limit where the Chandrasekhar-Clogston paramagnetic limit, $Z < Z_C = \Delta_0/\sqrt{2}$, applies.[17] Here $Z = g\mu_B B/2$ is the Zeeman coupling strength, μ_B is the Bohr magneton, and B is the magnetic induction.

For a constant level spacing spectrum, the single particle energy levels measured from the Fermi energy are $\xi_n = (n-\alpha)\delta$. Here $n = 0, \pm 1, \pm 2, \ldots$, and parity dependence appears in the quantity α which has the value 0 if the number of electrons N is odd and 1/2 if N is even, corresponding respectively to chemical potentials pinned at and half-way between energy levels. The gap equation for a model in which pairing interactions occur only between identical orbitals differs from its BCS theory counterpart only[12,16] in the discreteness of the quasiparticle level spectrum:

$$\frac{1}{\lambda} = \delta \sum_{n=1}^{M} \frac{1 - f(E_n + Z) - f(E_n - Z)}{E_n}, \tag{1}$$

where $E_n = \sqrt{\Delta^2 + \xi_n^2}$, λ is the dimensionless coupling constant and Δ is determined by solving these equations. The upper limit on this discrete sum comes from the energy cutoff used in BCS theory to model retarded attractive interactions and can be expressed in terms of Δ_0 using the bulk solution of the zero temperature gap equation

$$\Delta_0 = 2M\delta \exp(-1/\lambda). \tag{2}$$

Since, at available fields, the magnetic flux through an ultra-small grains will typically be much smaller than $\Phi_0 = \hbar c/2e$, coupling to orbital degrees of freedom[18] can normally be ignored. The electron spins still couple to the magnetic field B, however, splitting the single-particle energies, $\xi_n \to (n-\alpha)\delta \pm Z$.

For small superconducting particles it is essential that the occupation probabilities, f, in Eq. (1) be calculated in ensembles including states with only even or odd numbers of particles.[5] These differ from Fermi occupation probabilities only for levels close to the chemical potential and only for temperatures $k_B T \lesssim \delta$; at T=0 the even restriction has no effect and the odd restriction has only the effect of removing the orbital at the Fermi energy, which cannot be paired, from the gap equation. This model was first studied by von Delft et al.[12] to calculate the dependence of $\Delta(T)$ on δ. They found that $\Delta(T)$ remains close to its bulk value until δ is close to a critical value δ_c which is parity dependent: $\delta_c^{\rm odd}/\Delta_0 = \frac{1}{2}e^{\gamma} \simeq 0.89$ and $\delta_c^{\rm even}/\Delta_0 = 2e^{\gamma} \simeq 3.56$. Here $\gamma = 0.577215...$ is Euler's

constant. As $\delta \to \delta_c$ from below, the critical temperature and the zero temperature gap both tend to zero. Later Braun et al.[14] and Balian et al.[15] extended this work to the case of finite Zeeman coupling. Ref. 14 concentrated on comparison between theory and the experiments by Ralph et al.[8], finding good qualitative agreement. Ref. 15 concentrated on the influence of using parity dependent distribution functions at finite temperature, predicting significant qualitative effects for such quantities as the superconducting gap and the magnetization. Here we explore the full $T-Z$ phase diagram, examining dependences on parity and δ and focussing on the evolution of the $T-Z$ phase diagram toward its bulk limit result as δ decreases.

II. PHASE DIAGRAMS

The fundamental equation on which our calculations are based is the following coupling-constant-integration expression for the free-energy difference between superconducting and normal states:[19]

$$\Omega_s - \Omega_n = \frac{\Delta^2}{\lambda\delta} \\ -2\sum_{n=1}^{M}\int_0^{\Delta} d\Delta'\Delta' \frac{1-f(E'_n+Z)-f(E'_n-Z)}{E'_n}. \quad (3)$$

In Eq. (3) $E'_n = \sqrt{\xi_n^2+\Delta'^2}$. Since, in the second term on the right hand side of Eq. (3), Δ appears only in the upper limit of the coupling-constant integration, it is easy to verify that the gap equation, Eq. (1), is satisfied at extrema of the condensation energy $\Omega_s - \Omega_n$. A sufficient condition for superconductivity in this model is that $\partial_{\Delta^2}(\Omega_s-\Omega_n)|_{\Delta^2=0}$ be negative; this derivative changes sign along the surface in (Z,T,δ) space where the linearized ($\Delta^2 \to 0$) gap equation is satisfied. When the phase transition is continuous, this surface, $Z_2(T,\delta)$, is the boundary of the superconducting region. If, on the other hand, $\partial_{\Delta^2}(\Omega_s-\Omega_n)|_{\Delta^2=0}$ is positive the grain may still be in a superconducting phase if $\Omega_s-\Omega_n$ is negative at a finite value of Δ. In that case the phase boundary is of first order and the corresponding critical value of Z is denoted $Z_1(T,\delta)$.

Below we determine the functions $Z_2(T,\delta)$ and $Z_1(T,\delta)$, and thereby show how the phase diagram for bulk systems is generalized to systems with finite level spacing.

A. Normal state instability at $T=0$

It is instructive to start by considering $Z_2(T=0,\delta)$ which can be evaluated analytically by solving the linearized gap equation (1). To that end we note that at $T=0$ the factor $[1-f(\xi_n+Z)-f(\xi_n-Z)]$ in Eq. (1) equals zero if $\xi_n - Z$ is negative and otherwise equals one. Hence, as Z is increased an additional pair of states $(n\uparrow, n\downarrow)$, is blocked from pairing every time $\alpha + Z/\delta$ passes through an integer value. It follows that

$$Z_2(T=0,\delta) = (m-\alpha)\delta \quad (4)$$

where m is the largest integer for which

$$\sum_{n=m}^{M}\frac{1}{n-\alpha} = \psi(M+1-\alpha) - \psi(m-\alpha) > \frac{1}{\lambda}. \quad (5)$$

Here $\psi(x)$ is Euler's ψ function. Using $\psi(x) \sim \ln(x)$ for large arguments and replacing M using Eq. (2) we find that m is the largest integer for which

$$\delta/\Delta_0 < \frac{1}{2}\exp[-\psi(m-\alpha)]. \quad (6)$$

The resulting $Z_2(T=0,\delta)$ is plotted in Fig. 1 and Fig. 2 for even and odd N, respectively. In both cases the bulk value[20] $Z_2(T=0,\delta\to 0) = 1/2$ is recovered as can be verified by letting m become large in Eqs. (4) and (6). Rather than decresing steadily, $Z_2(T=0,\delta)$ oscillates around its $\delta \to 0$ limit with increasing δ. The maximum values of $Z_2(T=0,\delta)$ actually occur for $\delta \to \delta_c$ $(m=1)$; $Z_2^{\max}/\Delta_0 = e^{\gamma} \simeq 1.78$ for even N and $Z_2^{\max}/\Delta_0 = e^{\gamma}/2 \simeq 0.89$ for odd N. Both of these values exceed $Z_C/\Delta_0 = 1/\sqrt{2}$, and this analytic result thus establishes that the Chandrasekhar-Clogston limit[17] can be exceeded in the ultra-small particle limit and, as we see below, also over a broad range of small particle sizes. The decrease of Δ and of mean-field-theory critical temperatures with particle size is not accompanied by a corresponding decrease in the maximum allowed Zeeman coupling strength.

B. First-order Transition Phase Boundary at $T=0$

When Δ is finite, the pair-breaking condition ($Z > \sqrt{\xi_n^2+\Delta^2}$) is not satisfied until larger values of Z are reached compared to the $\Delta = 0$ case. Hence, at sufficiently low temperatures, states with finite Δ are favored over states with $\Delta \to 0$, causing the superconductor-normal transition to be of first order. This physics is much the same at finite δ and in the $\delta \to 0$ bulk thin film limit.

We consider first the ultra-small grain limit. At $T=0$ the integral in Eq. (3) can be evaluated analytically.

$$\Omega_s - \Omega_n = \frac{\Delta^2}{\lambda\delta} - 2\sum_{n=1}^{M}\{\max(E_n,Z) - \max(\xi_n,Z)\} \\ \simeq \frac{\Delta^2}{\delta}\ln(\delta/\delta_c) + \frac{\Delta^4}{4\delta^3}\zeta(3,\alpha) + 2(Z-Z_2). \quad (7)$$

The first form for the right hand side of Eq. (7) is exact whereas the second form only applies in the ultra-small

grain regime: $\xi_2 > Z > \xi_1$, $E_1 > Z$ and $\Delta/\delta \ll 1$. In Eq. (7), ζ is Riemann's Zeta Function; $\zeta(3,0) \simeq 1.2021$ and $\zeta(3,1/2) \simeq 8.4144$. Minimizing $\Omega_s - \Omega_n$ we find that $\Delta^2 = 2\delta^2 \ln(\delta_c/\delta)/\zeta(3,\alpha)$ and

$$Z_1(T=0,\delta) = Z_2(T=0,\delta) + \delta \frac{[\ln(\delta_c/\delta)]^2}{2\zeta(3,\alpha)} \tag{8}$$

for $\delta \to \delta_c$. This expression is plotted together with exact numerical evaluations of $Z_1(T=0,\delta)$ in Figs. 1 and 2 for even and odd N respectively. $Z_1(T=0,\delta)$ and $Z_2(T=0,\delta)$ become equal only as $\delta \to \delta_c$.

We notice in Fig. 1 that the exact numerical evaluation recovers the familiar Chandrasekhar-Clogston result in the bulk limit: $Z_1(T=0,\delta \to 0) = 1/\sqrt{2}\Delta_0$ is recovered for both even N and odd N. The exact numerical results for $Z_1(T=0,\delta)$ were obtained by evaluating $\Omega_s - \Omega_n$ as a function of Δ and locating zero-crossings of its minimum as Z is increased. In Fig. 3 we show the dependence of $(\Omega_s - \Omega_n)/N$ on Δ for four different values of δ at $(T=0, Z=0.65\Delta_0)$ for an even number of electrons. For $\delta/\Delta_0 = 1.4$ this corresponds to $Z < Z_2(\delta)$, but for the three lowest values of δ, $Z_2(\delta) < Z < Z_1(\delta)$ and the slope at $\Delta = 0$ is therefore positive. $\Omega_s - \Omega_n$ nevertheless becomes negative at a finite value of Δ, and in all cases the optimal value of Δ (for which $\Omega_s - \Omega_n$ has its minimum) is very close to the bulk value Δ_0. As shown by von Delft *et al.*,[12] only when δ is very close to δ_c does the optimal value diminish significantly. It is furthermore worth noticing that, as can easily be concluded from Eq. (7), the optimal value of Δ is independent of Z, for $Z < Z_1$.

Each time the number of Pauli blocked pairs decreases with increasing Δ, the free energy curve has an upward-pointing cusp as exemplified in Fig. 3 by the three smallest values of δ. The cusps are spaced more closely at smaller values of δ, but the overall envelopes of the three curves are rather similar. (The fourth curve has no cusps because neither normal nor superconducting states are spin-polairzed.) In a model with constant energy level spacings, as employed here, the minimum of $\Omega_s - \Omega_n$ always occurs with a minimum of blocked pairs, i.e. in the superconducting state the grain will have spin zero for even N and spin 1/2 for odd N.

C. Full $T-Z$ phase diagrams

At finite temperature both of the functions $Z_1(T,\delta)$ and $Z_2(T,\delta)$ are found by numerically analyzing $\Omega_s - \Omega_n$ as a function of Δ. In Fig. 4 we show the finite temperature version of the plots in Fig. 3. The cusps are thermally broadened and the condensation energies have diminished for all values of Z. The full T-Z phase diagram depends on both δ and electron-number parity. Examples at representative intermediate values of δ are presented in Figs. 5 and 6. The general picture is similar to the bulk case,[20] even as δ/Δ approaches one. At low temperature $Z_1(T,\delta) > Z_2(T,\delta)$ and the transition to the normal state is first order. At the transition Δ then drops abruptly from its $Z=0$ value, $\Delta(T,\delta,Z=0)$, to zero. At higher temperatures, $Z_1(T,\delta) = Z_2(T,\delta)$ and the transition is continuous. In that case, the free energy curves do not cross zero at finite Δ if their initial slope is positive.

Whereas $Z_1(T \to 0,\delta)$ only differs from its bulk value in the ultra-small limit, $Z_2(T \to 0,\delta)$ has a significant δ-dependence even for intermediate grain sizes. Although Z_2 doesn't correspond to a phase transition at low temperatures, it does have physical meaning as a supercooling curve, and has been successfully addressed experimentally in thin films[21] by measuring enhanced fluctuations in the neighborhood of Z_2.

III. DISCUSSION

Level spacings near the chemical potential in a real ultra-small grain will fluctuate[13] around the mean-value used in our idealized model. For an even number of electrons $\mu(T=0,Z=0)$ will fall between[22] two energy levels ϵ_a and ϵ_{a-1}. For an odd number $\mu(T=0,Z=0)$ will fall close to[22] a level ϵ_a. Since our results for $Z_2(T=0,\delta \to \delta_c)$ depend primarily on Pauli blocking of the first pair of levels, the main consequence of using a realistic spectrum are captured by identifying δ with $\epsilon_a - \epsilon_{a-1}$ for even N and $(\epsilon_{a+1} - \epsilon_{a-1})/2$ for odd N. As a consequence, like minimum grain sizes,[13] maximum Zeeman energies will have a broad distribution. Consequently, it is difficult to compare directly with specific data. Nevertheless our work appears to shed some light on the interpretation of both recent and older experiments.

In a pioneering early experiment, Giaever and Zeller[23] found a violation of the Chandrasekhar-Clogston limit which, to our knowledge, is still not fully explained. These authors studied tunneling through an ensemble of Sn grains with a narrow size distribution. Interpreting their measurements using a Coulomb blockade picture, they concluded that most grains retained a superconducting gap up to magnetic fields that exceeded the Chandrasekhar-Clogston limit. The more recent experiments by Ralph, Black, and Tinkham[8] also appear to find that the Chandrasekhar-Clogston limit can be exceeded. In the later tunneling experiments, a quasiparticle gap, is observed to decrease linearly with the Zeeman coupling strength Z. The linear dependence arises from the Zeeman splitting of quasiparticle energies and is consistent with the mean-field theory employed in this paper.[14] The linear decrease continues to Zeeman fields that exceed the Chandrasekhar-Clogston limit without the discontinuous drop which would be expected if Δ dropped abruptly to zero. However, this observation is made at a value of Δ_0/δ which is smaller than those for which the Chandrasekhar-Clogston limit is exceeded in a model

with equally spaced energy levels. The experiment could be explained by assumming that this particular sample happens to have a relatively large energy spacing at the Fermi energy.

The results presented in this paper are based on mean-field theory, and a few cautionary remarks concerning its validity are in order. For $T = 0$ and $Z \leq Z_2$, the mean-field condensation energy for $\delta \to \delta_c$ becomes microscopic: $\Omega_s - \Omega_n \to -\delta[\ln(\delta_c/\delta)]^2/\zeta(3,\alpha)$. Thermal fluctuations will therefore be important unless the temperature is well below the bulk critical temperature and quantum fluctuations[24] will be increasingly important as δ_c is approached. Clearly the ultrasmall grain in this regime will not exhibit anything approaching a true phase transition between normal and superconducting states. The phase boundaries found in mean-field-theory should be regarded as estimates for the localtions of crossovers which become more gradual as δ increases.

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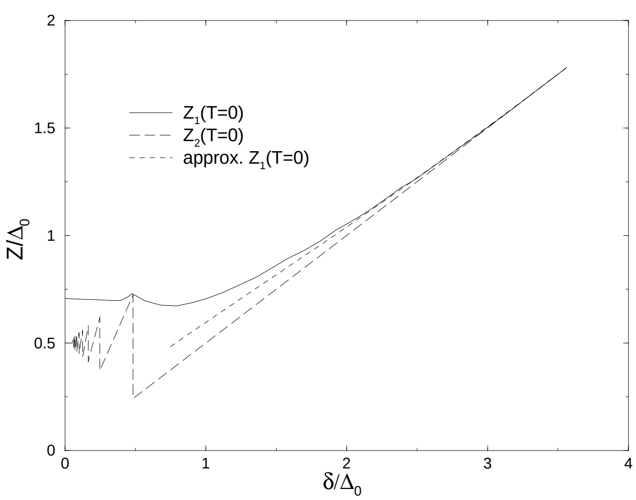

FIG. 1. The zero temperature limit of Z_1 (solid line) and Z_2 (long-dashed line) as a function of δ for an even number of electrons. The dashed line is the approximate expression (8) for Z_1 derived in the text. Z_2 can be evaluated analytically as explained in the text. The discontinuities in this curve occur at $\delta/\Delta_0 = 0.4821,\ 0.2475,\ 0.1659,\ 0.1247,\ ...$ and the corresponding minima and maxima are given by Eq. (4). The function $Z_1(T=0,\delta)$ is continous but it has discontinuities in its first derivative at a series of δ. This fact is further illustrated in Fig. 2.

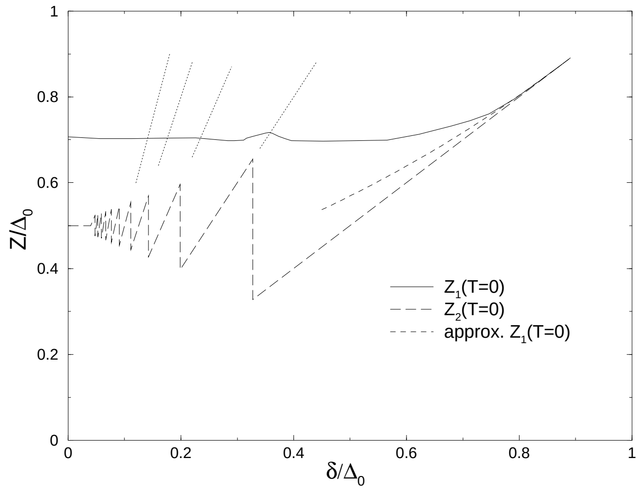

FIG. 2. As in Fig. 1 but for an odd number of electrons. The discontinuities in Z_2 occur at $\delta/\Delta_0 = 0.3276,\ 0.1987,\ 0.1424,\ 0.1109,\ \ldots$. As it is the case for even N (see Fig. 1), the function $Z_1(T=0,\delta)$ has discontinuities in its first derivative at a series of δ given by $Z_1(\delta) = (n-\alpha)\delta,\ n = 2,3,4,\ \ldots$, i.e. where extrapolations of Z_2 (indicated by dotted lines) cross Z_1. These cusps are a consequence of discontinuities of the first derivative of the normal state energy with respect to Z. In most cases, the cusps are too small see in this figure, however.

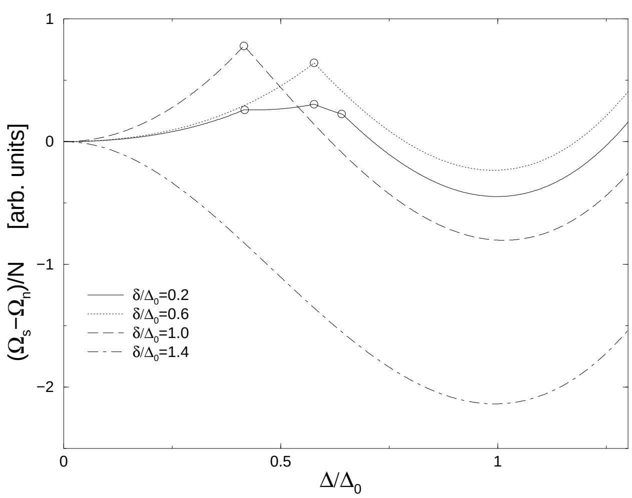

FIG. 3. The dependence of the free energy difference per particle $(\Omega_s - \Omega_n)/N$ on Δ at $(T=0, Z=0.65\Delta_0)$ for four different values of level spacing δ for an even number of electrons. The circles indicates cusps in the curves. The case $\delta/\Delta_0 = 1.4$ is special in the sense that it corresponds to Zeeman field below $Z_2(\delta)$ (see Fig. 1). For $Z > Z_2(1.4\Delta_0)$ this curve would also have a positive slope at $\Delta = 0$.

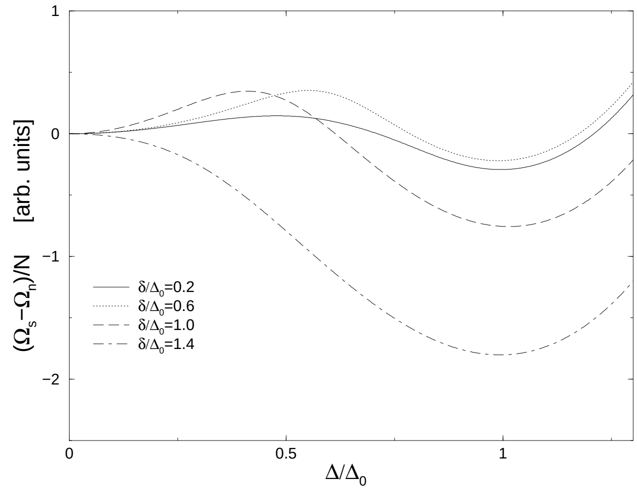

FIG. 4. The same as in Fig. 3 but at finite temperature $T/T_{c0} = 0.2$, where T_{c0} is the bulk critical temperature at $Z = 0$.

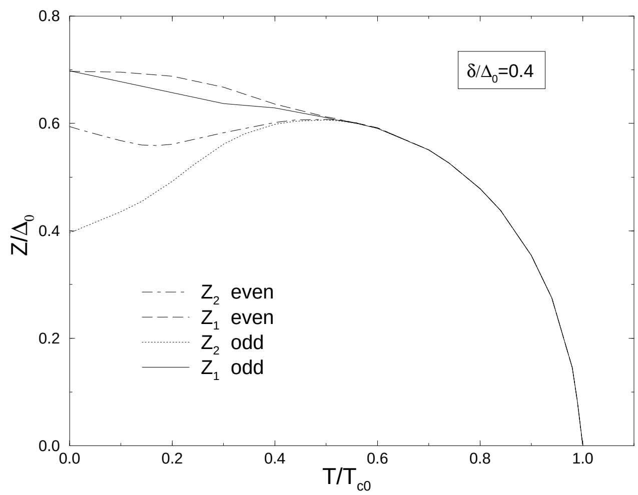

FIG. 5. The functions $Z_1(T)$ and $Z_2(T)$ for both even and odd numbers of electrons. This figure is for $\delta/\Delta_0 = 0.4$. Temperatures are expressed in terms of the bulk critical temperature T_{c0}. For $\delta/\Delta_0 = 0.4$ $Z_1(T=0)/\Delta_0$ is already close to its bulk value, $1/\sqrt{2}$. For both even and odd number of electrons the transition becomes first order near $T/T_{c0} = 0.56$, close to the corresponding bulk value. Z_2 shows the largest deviation from the bulk limit. For odd number of particles $Z_2(T=0,\delta) < Z_2(T=0,\delta \to 0)$ while for even number of particles $Z_2(T=0,\delta) > Z_2(T=0,\delta \to 0)$.

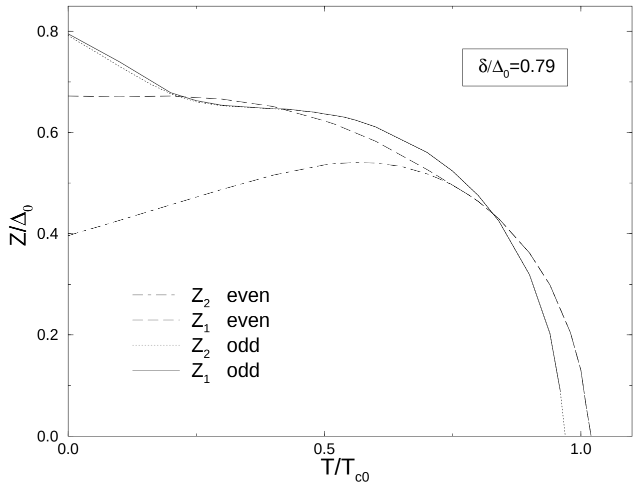

FIG. 6. The functions $Z_1(T)$ and $Z_2(T)$ for both even and odd numbers of electrons. This figure is for $\delta/\Delta_0 = 0.79$, a value sufficiently large to yield phase diagrams which differ substantially from their bulk counterparts. The transition becomes first order at $T/T_{c0} = 0.76$ for even N and at $T/T_{c0} = 0.44$ for odd N. This illustration also reflects the dependence of the critical temperature δ and parity discussed by by von Delft *et al.*[12]. For odd N T_c decreases monotonically with δ whereas for even N it increases up to about $\delta/\Delta_0 \sim 2$ before it decreases.